



Hydrogen and methane selectivity during alkaline supercritical water gasification of biomass with ruthenium-alumina catalyst

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ABSTRACT

Ruthenium supported on alpha-alumina spheres has been employed as a catalyst for the gasification of glucose and other biomass-related samples in supercritical water at 550 °C, 36 MPa, in a batch Inconel reactor. Most of the reactions were conducted in the presence of alkaline additives particularly sodium hydroxide and calcium oxide (hydroxide). In general, over 96% carbon gasification efficiencies (CGE) were achieved in the presence of Ru/Al₂O₃, while hydrogen gasification efficiencies (HGE) based on result-derived reaction stoichiometries reached 87% for glucose. Both HGE and CGE approached 100% for the sodium carboxylates. Without alkaline additives, Ru/Al₂O₃ converted glucose into gas product with average yields of 10.8 mol hydrogen/(kg of glucose), 8.6 mol methane/(kg of glucose) and 17 mol carbon dioxide/(kg of glucose), while carbon monoxide and C₂–C₄ hydrocarbons made up only 1 mol/(kg of glucose). However, when the ruthenium catalyst was used in combination with sodium hydroxide and calcium hydroxide, the selectivity towards hydrogen gas increased, with the complete removal of carbon dioxide. Similar yields of hydrogen (14.7 mol/kg of glucose) and methane (12.8 mol/kg of glucose) were obtained with CaO and Ru/Al₂O₃. Reactions of sodium carboxylates (formate and acetate) suggested that the ruthenium catalyst was capable of catalyzing the Sabatier reversible reaction in both the forward and backward directions. The yield of each gas was found to be dependent on the concentrations of methane, hydrogen and carbon dioxide in the reactor.

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1. Introduction

Biomass represents a natural store of energy, which can be harnessed in different forms for different uses. Large scale biomass use for energy production has many advantages particularly in view of depleting fossil resources and tackling climate change. In this regard, the conversion of biomass to energy carriers has become a topical research area. Thermochemical biomass conversion processes include well-established conventional technologies such as pyrolysis, gasification, liquefaction and incineration. In addition to these, hydrothermal gasification of biomass has become an active research topic over the last few years. The main components of the gas product from hydrothermal gasification of biomass include hydrogen, methane and carbon dioxide and some carbon monoxide [1–5]. This has been largely supported by the potential of hydrogen fuel gas as the world's cleanest energy carrier. Hence, hydrothermal gasification has focused mainly on hydrogen gas production. However, chemical energy storage and utilization in the form of methane is often seen as more commercially attractive

than hydrogen. Methane produced from renewable biomass would be readily fed into the existing infrastructure. Thermochemical production of methane involves a fast process, with consequent high conversion rates [6], compared to anaerobic digestion. Therefore, hydrothermal gasification of biomass to produce a syngas composed mainly of methane and hydrogen can become an important component of the world's future energy portfolio.

Synthetic natural gas (SNG) production via hydrothermal gasification (HTG) often involves the use of metal catalysts such as nickel and ruthenium; supported on alumina or silica [7–10]. Ruthenium and nickel catalysts have been widely used for methane production via the hydrogenation of carbon dioxide and/or carbon monoxide. Waldner and Vogel [11] reported the production of synthetic natural gas (SNG) from woody biomass by a catalytic hydrothermal process using a laboratory batch reactor suitable for high feed concentrations (10–30 wt %). Their work carried out at 300–410 °C and 12–34 MPa with a Raney nickel catalyst, produced a maximum methane yield of 0.33 (g of CH₄)/(g of wood), which corresponded to the thermodynamic equilibrium yield. They achieved complete carbon gasification efficiency over an extended reaction time of about 90 min. Stucki et al. [12] reported that between 60–70% of the heating value of microalgae (*Spirulina platensis*) could be recovered as methane during HTG at 400 °C in the presence of

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ruthenium catalysts with a high overall conversion approaching 100%. More recently, Haiduc et al. [13] demonstrated the hydrothermal gasification of the microalgae *Phaeodactylum tricornutum* to a methane-rich gas at a temperature range of 400 °C and pressure of 30 MPa, using ruthenium catalysts. Carbon gasification efficiency was high (68–74%) and the combined yields of C₁–C₃ hydrocarbon was 0.2 g/g of dry feed. The biomass-released sulfur was shown to adversely affect the Ru/C catalyst performance. Azadi et al. [14] reported that Raney-nickel catalyst produced about 13 mmol of gas per gram of glucose at 350 °C. The composition of the gas product was; 69 mol% carbon dioxide; 23 mol% hydrogen and 8.5 mol% methane, at 350 °C and a pressure of 6.2 MPa. Recently, Azadi et al. [15] also demonstrated the positive effects of the addition of alkali promoters to alpha-alumina-supported nickel catalyst at 380 °C during the catalytic gasification of a 2 wt% glucose solution. Under experimental conditions of the study, about 55 mol of gas was produced per kg of glucose, with carbon and hydrogen gasification efficiencies of 99% and 127% respectively.

In several publications, the present authors [16–18] and others, for example, Kruse et al. [19] and Sinag et al. [20] have shown that the addition of alkaline compounds during hydrothermal processing of biomass leads to favourable degradation of carbohydrate-rich biomass into gasifiable intermediates. In particular, the authors found that addition of sodium hydroxide and potassium hydroxide led to the formation of gasifiable simple alkali-metal carboxylates. Potentially, hydrogen/methane ratios of 5:1 could be achieved in the gasification of carbohydrate biomass in the presence of sodium hydroxide at a ratio of 1 g glucose per 1.2 g of sodium hydroxide. No carbon dioxide is found in the gas phase, as this is removed as soluble sodium carbonate [18]. The high concentration of alkali, though beneficial for high-purity hydrogen production, can significantly affect the cost of the gasification process. A reduction in the amount of alkaline additives or the use of cheaper compounds such as calcium oxide and calcium hydroxide coupled with the use of stable metal catalysts may lower the cost of this process.

The chemistry of hydrogen production from hydrothermal biomass gasification appears to depend mainly on the water-gas shift reaction. Methane formation during alkaline hydrothermal gasification has been found to mainly depend on the decomposition reaction of metal acetates [16,21,22]. In non-alkaline hydrothermal environments, methane formation has been found to occur via methanation reactions in the presence of some supported metal catalysts [7,8].

In this work, the effect of a ruthenium/alumina catalyst has been studied during the alkaline gasification of some biomass samples and biomass model compounds. The alkaline additives used include sodium hydroxide, calcium hydroxide and calcium oxide. The effect of the catalyst on the hydrothermal reactions of sodium formate and sodium acetate was also studied. In each case, the composition analyses of the gas products have been carried out and used to explain the effect of the catalyst on the main gas components present. In addition, the stability of the ruthenium catalyst was examined.

2. Experimental

2.1. Materials

Glucose, cellulose, xylan, sodium acetate and sodium formate, sodium hydroxide, sodium carbonate, calcium hydroxide were all purchased from Sigma-Aldrich, UK. The CHNS-O analysis of the sawdust gave the following compositions; carbon, 48.3 wt%; hydrogen, 5.67 wt%; oxygen, 44.3 wt% and sulphur, 0.73 wt%. Ruthenium-alpha alumina catalyst was supplied by Catal Limited,

a UK-based SME and used as received. The nominal loading of ruthenium impregnated on 2–4 mm diameter alumina spheres was 5 wt%. The catalyst has a specific surface area of 21 m² g⁻¹ and an average pore size of 1.5 µm. The reactor used was a 75 ml batch Inconel reactor obtained from Parr Inc. U.S.A. Details of the reactor have been provided in several previous publications [17,18].

2.2. Procedure

In each case, 1.0 g of feed material (glucose, cellulose, xylan, sodium acetate or sodium formate) was loaded into the reactor containing 20 ml of distilled water. Where required, a known weight of alkaline compound (sodium hydroxide, calcium hydroxide or calcium oxide) was then added and mixed with the biomass and water in the reactor. To compare the effects of the alkaline compounds on the gasification tests, 1.20 g each of sodium hydroxide and calcium oxide, corresponding to 1.50 M NaOH and 1.07 M CaO, were used in separate alkaline gasification tests. In addition, since CaO would be transformed to Ca(OH)₂ on addition to water, one test was performed using 1.07 M Ca(OH)₂. The lower molar concentrations of Ca(OH)₂ and CaO used here was due to the consideration that both calcium compounds would form insoluble calcium carbonate by reacting with carbon dioxide in the gas products, thereby leading to reactor plugging and other complications. For tests involving ruthenium-alumina (Ru/Al₂O₃) catalyst, 1.0 g of the catalyst was placed in a wire mesh suspended inside the reactor. The reactor was closed, purged with nitrogen gas for 5 minutes and sealed. The reactor was heated quickly at a rate of 30 °C min⁻¹ up to 550 °C, such that the reaction temperature was reached after just 18 minutes; giving corresponding pressures of between 36 and 40 MPa. Once the designated temperature was reached, the reaction was allowed to stabilize for 10 minutes, after which the reactor was withdrawn from the heater and cooled rapidly with compressed air.

2.3. Gas analyses

Once cooled to room temperature, the pressure and temperature readings were noted prior to sampling the gas for analysis. The analytical equipment and procedure used for gas analysis have been previously reported in details [18,23]. The compositions of the gas products were obtained in mole percent and used to calculate the yields of the components.

2.4. Liquid analyses

The liquid effluents were analyzed for total organic carbon (TOC) and inorganic carbon (IC) which was used to indicate the extent of conversion of the feed materials during the hydrothermal gasification process. The instrument used was a Hach-Lange IL550 TOC-TN analyzer fitted with two NDIR held at 800 °C. The instrument was operated in the differential TOC determination mode, in which the same sample was analyzed consecutively for total carbon (TC) and total inorganic carbon (TIC). The difference between the TC and TIC was recorded as TOC. The analyzer was set up to make four determinations (*n* = 4) on each sample and the average results used. Typical standard deviation of replicate determinations ranged from 0.2 to 2%.

2.5. Solid analyses

In experiments, where calcium oxide was used, the formation of insoluble calcium carbonate was observed. In these cases, the insoluble solids were obtained after filtration and dried in an oven to a constant weight. The solids were pulverized and analyzed on thermogravimetric analyzer to determine the inorganic carbon content. The instrument used was a Metler Toledo TGA/DSC 1 Star System.

Approximately 20 mg (± 0.50 mg) was loaded into the sample pan and heated under nitrogen atmosphere from 50 °C to 1000 °C at a constant rate of 20 °C min⁻¹. Samples of pure CaCO₃ and Ca(OH)₂ were also analyzed as standards. Ca(OH)₂ was included because of the expectation that CaO, once added to water would be converted to Ca(OH)₂. In addition, a selection of the solid residues obtained after the gasification experiments were analyzed using X-ray Diffractometer (XRD) for the existence of crystalline products. The description of XRD equipment has been fully detailed in a previous paper [16].

3. Results and discussions

3.1. Gas products distribution

The distributions of gas products obtained after the supercritical water gasification of the feed materials are presented in Table 1. Many experiments were carried out with glucose as a biomass model compound. The table presents the amount of gas produced (in g) and the normalized gas product distribution in mole percent after the removal of nitrogen purge gas from the analyses results.

3.1.1. Gasification of glucose

Results show that without any catalyst, 0.48 g of gas product, equivalent to 12.3 mol gas/(kg of glucose), was obtained from hydrothermal gasification of glucose. The gas product was composed of 66 mol% carbon dioxide, 12 mol% hydrogen, 15.4 mol% carbon monoxide, 3.38 mol% methane and 3.16 mol% C₂–C₄ hydrocarbon gases. For catalytic experiments, two sets of duplicate experiments were firstly carried out with Ru/Al₂O₃; in experiment #2, the catalyst was mixed with the glucose solution, while in experiment #3, the Ru/Al₂O₃ catalyst was suspended in the wire gauze. No significant differences were observed in the reaction products from the two experiments. However, the catalyst experienced about 9–11% weight loss when it was mixed with the glucose solution but remained fairly physically stable when suspended.

Subsequent experiments were thus carried out by suspending the Ru/Al₂O₃ in the wire mesh as described earlier. Results show that in the two experiments with the ruthenium catalyst, gas production increased significantly reaching up to 0.95 g (37.1 mol gas/(kg of glucose)). No significant tar formation was observed. Char formation was not evident on the catalyst itself but the wire gauze appeared darker, probably as result of carbon deposition. The amount of char deposited on the gauze was obtained by weighing the dried gauze before and after experiment. The average composition of the gas products obtained from these two experiments were 29 mol% hydrogen, 21.6 mol% of methane and 48.3 mol% of carbon dioxide, while carbon monoxide and C₂–C₄ hydrocarbons made up only 2.02 mol%. Compared to the gasification of glucose without the catalyst, these results show evidence of the selectivity of the Ru/Al₂O₃ catalyst towards methane and hydrogen formation.

Fig. 1 shows the yields of the different gas components in mol/kg of glucose during the gasification tests with Ru/Al₂O₃ and sodium hydroxide. Without any catalyst, the total yield of gas was 13.2 mol/kg of glucose, comprising hydrogen and methane yields of 1.48 mol/kg of glucose and 0.5 mol/kg, respectively. The balance was mainly carbon dioxide (68%) and some carbon monoxide (10.1%). However, with the Ru/Al₂O₃ alone, hydrogen yield increased to about 10 mol/kg, and methane increased to 8.6 mol/kg and about 17 mol/kg of CO₂ was produced. The overall gasification of glucose with the ruthenium catalyst alone achieved here was comparable to the results achieved recently by Stucki et al. [12], who achieved nearly complete hydrothermal gasification of the micro-algae, *Spirulina platensis*. Also, Elliot and Hart [24] reported

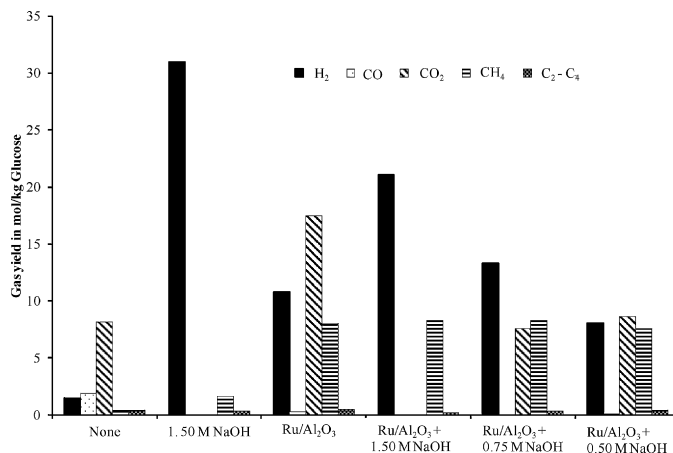


Fig. 1. Effect of sodium hydroxide concentration and Ru/Al₂O₃ on gas yields.

gasification efficiencies of over 99% in terms of percentage COD removal for different components of food wastes.

In the presence of 1.50 M NaOH alone, Table 1 shows that 37.1 mol gas/kg of glucose was obtained in the gas phase, which contained 94 mol% hydrogen gas, 4.94 mol% methane and 1.06 mol% C₂–C₄ gases. Due to the dominance of hydrogen gas, the total weight of gas obtained was only 0.10 g. This result translated to hydrogen production of 31.1 mol/kg of glucose (62.2 g of H₂/kg of glucose), with methane at only 1.63 mol/kg and no CO₂ was detected in the gas phase. However, considering that carbon dioxide would have been produced but removed as carbonate, the amount of inorganic carbon (IC) obtained from the analysis of the aqueous phase showed that 34.1 mol of carbon/kg of glucose was in the aqueous phase. Since one mole of sodium carbonate contains one mole of carbon dioxide, the total amount of gas produced during the gasification of glucose in the presence of 1.50 M NaOH was 71.2 mol/kg of glucose. When the same concentration of NaOH was used in the presence of 1.0 g of Ru/Al₂O₃ catalysts, the gas product was 58.5 mol gas/kg of glucose. This time the hydrogen yield reduced to 21.3 mol/kg of glucose, while methane production increased nearly eight times to 8.3 mol/kg, along with complete removal of carbon dioxide. The amount of carbon dioxide obtained as carbonate was 28.9 mol/kg of glucose. Thus the decreases in the yields of hydrogen and carbon dioxide (as carbonate) could be attributed to methanation reaction between these two gases, in the presence of the ruthenium catalyst.

Subsequently, the NaOH concentrations were reduced to 0.75 M and 0.5 M, respectively, while the catalyst loading and glucose loading were kept constant at 1.0 g each. Results showed that with 0.75 M NaOH, the amount of gas product increased to 0.51 g and reached 0.54 g when glucose was reacted 0.50 M NaOH solution in the presence of the ruthenium catalyst. Interestingly, the mole percent of these three gases were similar (about 30 mol%) when NaOH concentration was 0.5 M. The yields of hydrogen reduced to 13.3 mol/kg and 8.05 mol/kg, respectively with decreasing NaOH concentration. On the other hand, the yield of methane remained fairly constant at about 8 mol/kg of glucose, while CO₂ in the gas phase increased to around 8 mol/kg of glucose. Meanwhile, the amount of carbonate produced decreased to 16.7 mol/kg and 12.4 mol/kg with 0.75 M and 0.50 M NaOH, respectively. The increase in the weight of gas produced with decreasing NaOH concentration was attributed to the increase in the proportion of carbon dioxide in the gas phase. The increase in the yield of carbon dioxide with decreasing NaOH concentration was due to the decreasing ability of the alkali to completely remove carbon dioxide as carbonate. However, the increase in the yield of methane would

Table 1

Gas yields and percentage gas compositions during catalytic supercritical water gasification of various biomass samples.

S/N	Sample	Catalysts	Gas yield (g)	Gas composition, mol%				
				H ₂	CO	CO ₂	Methane	C ₂ –C ₄ gases
1	Glucose	None	0.48	12.0	15.4	66.1	3.38	3.15
2	Glucose	^a Ru/Al ₂ O ₃	0.95	29.0	0.73	47.3	21.6	1.29
3	Glucose	Ru/Al ₂ O ₃	0.95	28.7	0.72	47.1	22.2	1.28
4	Glucose	^b Ru/Al ₂ O ₃ 2nd Use	0.94	38.3	0.23	42.5	17.6	1.37
5	Glucose	^b Ru/Al ₂ O ₃ 3rd Use	0.90	40.2	0.23	41.6	16.4	1.57
6	Glucose	1.50 M NaOH	0.10	94.0	nd	nd	4.94	1.06
7	Glucose	Ru/Al ₂ O ₃ + 1.50 M NaOH	0.18	71.2	nd	nd	28.0	0.84
8	Glucose	Ru/Al ₂ O ₃ + 0.75 M NaOH	0.51	47.1	nd	22.2	29.3	1.40
9	Glucose	Ru/Al ₂ O ₃ + 0.5 M NaOH	0.54	32.8	0.07	34.3	31.0	1.74
10	Glucose	Ru/Al ₂ O ₃ + 1.07 M Ca(OH) ₂	0.25	64.8	2.54	7.21	21.7	3.69
11	Glucose	1.2 g CaO	0.08	81.8	7.78	nd	5.80	4.57
12	Glucose	Ru/Al ₂ O ₃ + 1.07 M CaO	0.41	49.7	nd	5.75	43.1	1.35
13	Glucose	^b Ru/Al ₂ O ₃ 2nd Use + 1.07 M CaO	0.31	53.1	0.28	5.83	39.5	1.27
14	Glucose	^b Ru/Al ₂ O ₃ 3rd Use + 1.07 M CaO	0.25	56.3	0.41	5.76	36.2	1.33
15	Glucose	^c Ru/Al ₂ O ₃ 2nd Use + 1.07 M CaO	0.22	68.5	0.68	7.50	21.1	2.22
16	Xylan	Ru/Al ₂ O ₃	0.75	32.3	0.89	46.9	18.0	1.87
17	Xylan	Ru/Al ₂ O ₃ + 1.07 M CaO	0.28	54.3	5.26	nd	38.0	2.44
18	Sawdust	Ru/Al ₂ O ₃	0.72	24.6	1.21	35.3	37.7	1.22
19	Sawdust	Ru/Al ₂ O ₃ + 1.07 M CaO	0.21	52.4	4.86	1.37	38.5	2.88
20	Cellulose	Ru/Al ₂ O ₃	0.77	27.8	1.42	47.2	22.0	1.58
21	Cellulose	Ru/Al ₂ O ₃ + 1.07 M CaO	0.17	45.8	1.97	nd	50.3	1.88
22	HCOONa	None	0.24	77.0	0.42	22.4	0.11	nd
23	HCOONa	Ru/Al ₂ O ₃	0.24	59.2	0.57	15.4	24.6	nd
24	CH ₃ COONa	None	0.46	9.63	nd	29.6	61.6	nd
25	CH ₃ COONa	None	0.45	10.4	nd	30.0	59.6	nd
26	CH ₃ COONa	Ru/Al ₂ O ₃	0.43	37.5	nd	23.4	39.1	nd
27	CH ₃ COONa	Ru/Al ₂ O ₃	0.42	37.5	nd	22.5	40.0	nd

^a Ruthenium catalyst mixed with sample slurry.^b Catalyst reused after calcination.^c Catalyst reused without calcination

still indicate the possible role of the Ru/Al₂O₃ catalysts towards methanation reactions.

In order to make alkaline hydrothermal gasification more attractive, cheaper alkaline materials such as calcium oxide (CaO) may be used. Although, it must be pointed out that the poor solubility of both calcium hydroxide and calcium carbonate (final product) can easily pose a different problem during continuous operation. In this present study, CaO was used in place of NaOH for some gasification experiments. In such experiments, 1.20 g of CaO, corresponding to 1.07 M CaO, was applied. It was expected that all of the CaO would be converted to the hydroxide upon addition into water to produce 1.59 g of Ca(OH)₂ [CaO + H₂O → Ca(OH)₂]. In addition, one test experiment was carried out with 1.59 g of pure Ca(OH)₂ (1.07 M concentration) to compare results.

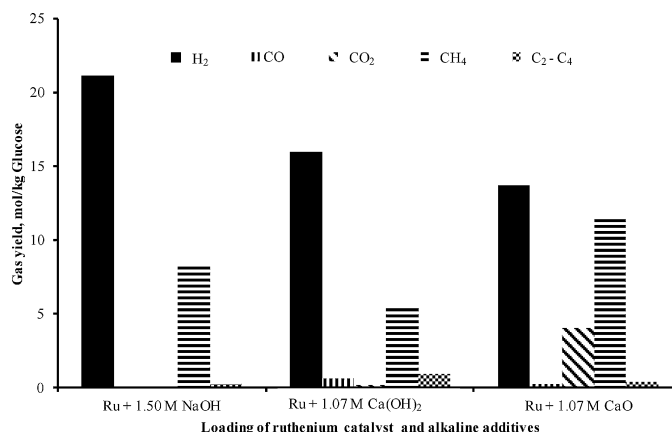
Results showed that when 1.07 M CaO alone was used only 12.4 mol/kg of gas-phase product, dominated by hydrogen, was obtained from glucose. The total gas product, including both gas-phase products and carbonates (solid and liquid residuals) was 30.1 mol/kg of glucose. However, in the presence of Ru/Al₂O₃ catalyst and 1.07 M CaO, total gas-phase product was 29.6 mol/kg of glucose, comprising mainly hydrogen, methane and CO. No carbon dioxide was detected in the gas phase but 22.3 mol of carbon/kg of glucose was found as carbonate, mainly in the solid product. Hence, a total gas yield of 52 mol/kg glucose was obtained from the use of Ru/Al₂O₃ and CaO. This was however less than the gas yield from the test with sodium hydroxide and Ru/Al₂O₃ catalyst. With 1.07 M calcium hydroxide (Ca(OH)₂) and the ruthenium catalyst, the yield of gas phase products decreased to 24.7 mol/kg. Total gas yield, considering the amount of carbon found in solid and liquid products as carbonates, was 47.0 mol/kg of glucose.

Therefore the total yield of gas products (including as carbonate) from the use of Ru/Al₂O₃ and the alkaline additives was in the order: NaOH > CaO > Ca(OH)₂. In addition, Fig. 2 compares the yields of gas-phase products obtained from the catalytic gasification of glucose with Ru/Al₂O₃ in the presence of the three alkaline

additives; NaOH, Ca(OH)₂ and CaO. The ratio of hydrogen production among the three alkaline additives was 1½:1½:1, while the ratio of methane production was 1½:1:2 for NaOH, Ca(OH)₂ and CaO, respectively. This showed that the reaction in the presence of NaOH produced more hydrogen than the two other additives. At the same time, CaO gave the best methane yield. In addition, with NaOH the ratio of hydrogen to methane was 2.5; with Ca(OH)₂, the ratio was 2.97, while with CaO, hydrogen methane ratio was 1.12. Hence, while NaOH and Ca(OH)₂ exhibited higher selectivity towards hydrogen, CaO showed nearly equal selectivities towards both hydrogen and methane in the presence of Ru/Al₂O₃.

3.1.2. Catalyst reuse

The ability of reusing the ruthenium catalyst for the gasification work was tested by a series of experiments shown in Table 1. After an initial experiment with fresh Ru/Al₂O₃, the used catalyst

**Fig. 2.** Effect of different alkaline additives on gas yields.

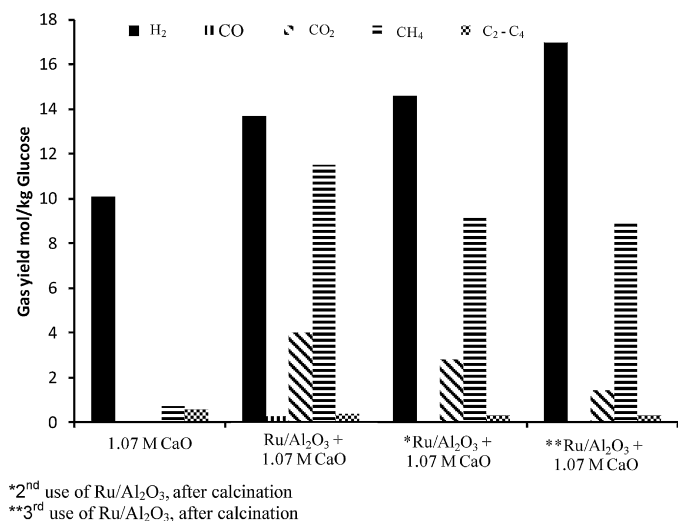


Fig. 3. Catalyst reuse and its effect on gas yields and composition.

was dried at 105 °C in an oven, calcined in a muffle furnace at 500 °C overnight and used in experiment #13. Further, the re-used catalyst was also re-calcined under the same conditions for a third use in experiment #14. Experiment #15 represents a situation where a used ruthenium catalyst was re-used without calcination. In all these cases, the catalyst was used in the presence of calcium oxide only. Fig. 3 shows the yields of gases obtained during these re-usability tests. An obvious trend observed is the increasing selectivity of the catalyst towards hydrogen production, while methane production showed a decreasing trend, particularly after first use. The increasing hydrogen production could not, arguably, be attributed to the effect of CaO only, since as shown in Fig. 3, hydrogen production (mol/kg) was lower with CaO alone than with any combinations of CaO with Ru/Al₂O₃.

Ruthenium catalyst alone was re-used twice more as presented in experiments #4 and #5 in Table 1 and the results suggest similar trends on increasing hydrogen selectivity. Hence, there is some evidence to suggest the involvement of the ruthenium catalyst in the observed changes in selectivities towards hydrogen to the disadvantage of methane. Some researchers [25,26] have reported phase changes of the alumina support, and even its conversion to aluminum hydroxide (or γ -bohmite) under hydrothermal conditions. Although Elliott et al. [25] reported that alpha- alumina was stable within the hydrothermal conditions of their research; they added that such stability was tenuous since the observed stability could be affected under a different set of hydrothermal conditions. Further work would be carried out to investigate the reasons behind these changes observed in the selectivities of product gases with repeated use of the Ru/Al₂O₃ catalyst in this present study.

3.1.3. Gasification of real biomass

Catalytic gasification of separate samples of xylan, sawdust and cellulose as representative biomass was attempted. Duplicate experiments were carried out with Ru/Al₂O₃, and in combination with CaO. The results show significant gas production with Ru/Al₂O₃ alone from all these samples, with high selectivities for hydrogen and methane production. On addition of CaO, the amount of gas produced, similarly decreased due to the removal of carbon dioxide but the yields of methane and hydrogen improved. Fig. 4 shows the yields of gas-phase products obtained during these experiments expressed in mol of gas/kg of feed. Although, xylan gave the lowest hydrogen and methane yields, overall results obtained from these samples showed similar trends to those of glucose. This suggests that the ruthenium catalyst could be effective for gasifying different types of biomass.

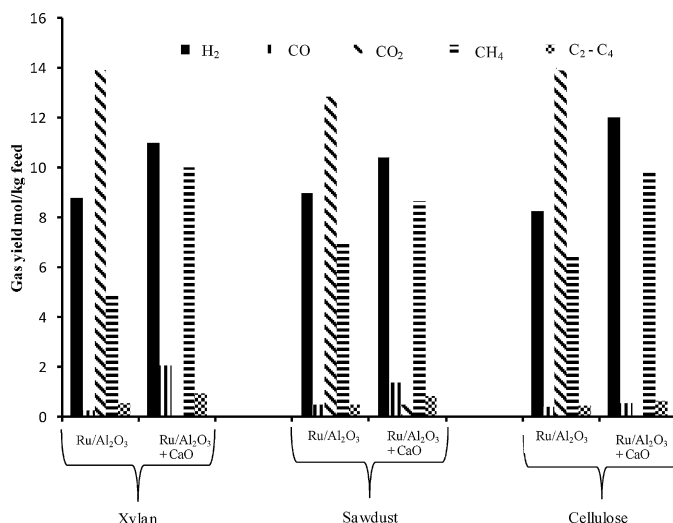


Fig. 4. Effect of Ru/Al₂O₃ and CaO on gas yields.

3.1.4. Reactions of sodium carboxylates

To effectively investigate the effect of the ruthenium catalyst on the gas products, experiments were conducted with sodium acetate and sodium formate whose hydrothermal reaction products had previously been studied and reported [18,27]. Onwudili and Williams [18] showed that simple sodium carboxylates such as sodium acetate and sodium formate react under hydrothermal conditions to produce methane and hydrogen gas, respectively. In similar work, Fischer et al. [28] also reported that higher carboxylates, such as butyric acid and 3-hydroxybutyrate decomposed under supercritical water condition to produce their corresponding C₃ hydrocarbons. In this work, both sodium acetate and sodium formate were independently reacted in supercritical water in the absence and presence of Ru/Al₂O₃. Results in Table 1 show that no significant changes in the total amount of gases produced occurred during these reactions. Without the Ru/Al₂O₃, the gas products from sodium formate comprised of hydrogen and carbon dioxide, while sodium acetate produced methane, carbon dioxide and almost negligible hydrogen as expected [18].

Although, the use of Ru/Al₂O₃ did not introduce new components into the gas products, it however, appeared to have significantly altered the compositional distribution of the gases. The mole percent compositions of the gas-phase products from both sodium formate and sodium acetate are presented in Table 1. These results are corroborated by Fig. 5, which presents the

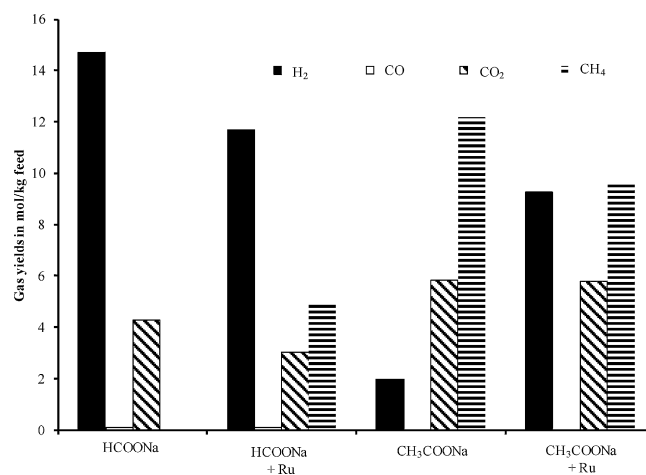


Fig. 5. Effect of Ru/Al₂O₃ on sodium formate and sodium acetate.

Table 2

Hydrogen gasification efficiency (HGE) from catalytic supercritical water gasification of biomass.

Sample	Catalysts	Hydrogen	Methane	C ₂ –C ₄	Total %	
					HGE1	HGE2
Glucose	None	3.80	2.14	3.22	9.16	6.58
Glucose	^a Ru/Al ₂ O ₃	27.6	41.1	4.09	72.8	64.5
Glucose	Ru/Al ₂ O ₃	28.2	39.7	4.23	72.2	64.0
Glucose	^b Ru/Al ₂ O ₃ 2nd Use	32.5	36.5	3.25	72.3	64.1
Glucose	^b Ru/Al ₂ O ₃ 3rd Use	34.3	35.2	3.21	72.7	64.4
Glucose	1.50 M NaOH	89.3	9.39	2.68	101	72.9
Glucose	Ru/Al ₂ O ₃ + 1.50 M NaOH	54.1	42.6	2.08	98.8	87.5
Glucose	Ru/Al ₂ O ₃ + 0.75 M NaOH	34.2	40.8	3.22	78.2	69.4
Glucose	Ru/Al ₂ O ₃ + 0.5 M NaOH	20.6	39.0	3.61	63.2	56.0
Glucose	Ru/Al ₂ O ₃ + 1.07 M Ca(OH) ₂	41.1	40.4	3.72	85.2	75.5
Glucose	1.2 g CaO	25.9	3.67	4.58	34.2	30.3
Glucose	Ru/Al ₂ O ₃ + 1.07 M CaO	37.8	57.7	3.67	99.2	87.9
Glucose	^b Ru/Al ₂ O ₃ 2nd Use + 1.07 M CaO	34.6	51.8	2.95	89.4	79.2
Glucose	^b Ru/Al ₂ O ₃ 3rd Use + 1.07 M CaO	35.7	46.0	2.90	84.5	74.9
Glucose	^c Ru/Al ₂ O ₃ 2nd Use + 1.07 M CaO	43.4	26.8	4.63	74.8	66.3
Xylan	Ru/Al ₂ O ₃	28.0	27.3	4.63	59.9	53.1
Xylan	Ru/Al ₂ O ₃ + 1.07 M CaO	30.1	37.6	4.41	72.2	64.0
Sawdust	Ru/Al ₂ O ₃	31.0	35.8	3.76	70.6	62.6
Sawdust	Ru/Al ₂ O ₃ + 1.07 M CaO	36.0	40.4	4.86	81.3	72.1
Cellulose	Ru/Al ₂ O ₃	33.6	29.7	4.06	67.3	59.7
Cellulose	Ru/Al ₂ O ₃ + 1.07 M CaO	37.5	40.8	4.16	82.5	73.1
HCOONa	Ru/Al ₂ O ₃	109	85.0	nd	194	97.6
HCOONa	None	190	0.55	nd	191	95.6
CH ₃ COONa	Ru/Al ₂ O ₃	47.9	99.9	nd	148	98.8
CH ₃ COONa	Ru/Al ₂ O ₃	46.9	100	nd	147	98.2
CH ₃ COONa	None	10.7	137	nd	148	98.7
CH ₃ COONa	None	11.8	136	nd	148	98.7

^a Ruthenium catalyst mixed with sample slurry.^b Catalyst reused after calcination.^c Catalyst reused without calcination.

yields of the component gases in mol/kg of individual carboxylate compound. With the ruthenium catalyst, significant increase in methane yield was found during the reaction of sodium formate, while enhanced hydrogen production was also obtained during the reaction of sodium acetate. For instance, during the

gasification of sodium formate, methane yield increased from 0.02 mol/kg without the catalyst to 4.9 mol/kg with the catalyst. Without the catalyst, hydrogen yield was 14.7 mol/kg, which was almost the theoretical yield expected from sodium formate. However, in the presence of the ruthenium catalyst, hydrogen yield

Table 3

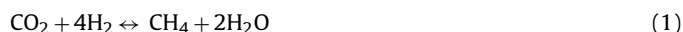
Carbon gasification efficiency (CGE) from catalytic supercritical water gasification of biomass.

Sample	Catalysts	CO	CO ₂	Methane	C ₂ –C ₄	IC (Aqueous)	IC (Solid Cake)	Total %
Glucose	None	4.98	21.4	1.10	2.82	1.95	nd	32.3
Glucose	^a Ru/Al ₂ O ₃	0.71	70.7	21.0	3.14	0.20	nd	95.8
Glucose	Ru/Al ₂ O ₃	0.73	71.0	21.2	3.11	0.15	nd	96.2
Glucose	^b Ru/Al ₂ O ₃ 2nd Use	0.42	73.2	19.3	3.33	0.22	nd	96.5
Glucose	^b Ru/Al ₂ O ₃ 3rd Use	0.41	74.1	18.5	3.23	0.20	nd	96.4
Glucose	1.50 M NaOH	nd	nd	4.80	2.38	89.4	nd	96.6
Glucose	Ru/Al ₂ O ₃ + 1.50 M NaOH	nd	nd	21.8	1.55	75.8	nd	99.1
Glucose	Ru/Al ₂ O ₃ + 0.75 M NaOH	nd	20.0	21.8	2.38	43.7	nd	87.9
Glucose	Ru/Al ₂ O ₃ + 0.5 M NaOH	0.05	31.4	19.9	2.69	32.4	nd	86.4
Glucose	Ru/Al ₂ O ₃ + 1.07 M Ca(OH) ₂	1.65	4.67	23.3	6.44	0.39	58.0	94.4
Glucose	1.2 g CaO	2.52	nd	1.88	3.79	0.44	45.9	54.5
Glucose	Ru/Al ₂ O ₃ + 1.07 M CaO	nd	4.48	33.5	2.69	0.26	58.7	99.7
Glucose	^b Ru/Al ₂ O ₃ 2nd Use + 1.07 M CaO	0.19	4.02	26.4	2.19	0.31	63.6	96.8
Glucose	^b Ru/Al ₂ O ₃ 3rd Use + 1.07 M CaO	0.20	3.74	23.5	2.18	0.35	66.7	96.7
Glucose	^c Ru/Al ₂ O ₃ 2nd Use + 1.07 M CaO	0.44	4.85	13.7	3.59	0.48	71.1	94.1
Xylan	Ru/Al ₂ O ₃	0.70	65.4	20.1	3.62	1.09	nd	90.9
Xylan	Ru/Al ₂ O ₃ + 1.07 M CaO	3.41	2.63	24.6	3.79	0.50	63.2	98.2
Sawdust	Ru/Al ₂ O ₃	1.16	65.4	21.6	2.89	0.87	nd	91.9
Sawdust	Ru/Al ₂ O ₃ + 1.07 M CaO	2.52	2.19	26.0	3.92	0.81	63.2	98.7
Cellulose	Ru/Al ₂ O ₃	1.11	65.2	26.6	3.08	0.44	nd	96.4
Cellulose	Ru/Al ₂ O ₃ + 1.07 M CaO	1.35	nd	28.9	3.63	0.63	64.5	99.0
HCOONa	None	0.53	14.3	23.0	nd	60.3	nd	98.1
HCOONa	Ru/Al ₂ O ₃	0.52	27.7	0.14	nd	69.8	nd	98.2
CH ₃ COONa	None	nd	20.0	33.4	nd	46.0	nd	99.4
CH ₃ COONa	None	nd	18.8	33.4	nd	46.9	nd	99.1
CH ₃ COONa	Ru/Al ₂ O ₃	nd	22.0	45.7	nd	30.8	nd	98.5
CH ₃ COONa	Ru/Al ₂ O ₃	nd	22.8	45.3	nd	30.4	nd	98.6

^a Ruthenium catalyst mixed with sample slurry.^b Catalyst reused after calcination.^c Catalyst reused without calcination.

decreased to 11.7 mol/kg, corresponding to a significant methane formation. Considering sodium acetate, complete conversion to methane was achieved without the catalyst. However, the yield of hydrogen increased from 1.98 mol/kg to 9.26 mol/kg in the presence of Ru/Al₂O₃. The increase in hydrogen production also corresponded to a decrease in methane yield. As shown in Tables 1–3, the experiments with sodium acetate were repeated twice and gave consistent results, with standard deviations ranging from 0.15–3.1%.

From the work with these sodium carboxylates, there is a strong suggestion of the role of the ruthenium catalyst to catalyze both methane formation via hydrogenation of carbon dioxide, as well as the formation of hydrogen via methane reforming. In particular, ruthenium-based catalysts have been reported [29,30] to be very effective in the reversible Sabatier reaction shown below;



The reverse reaction of the equation above represents the methane-steam reforming reaction. Laboratory research on hydrothermal processes attempt to mimic such natural hydrothermal environments. Recently, Taran et al. [31] suggested that the presence of methane- and hydrogen-rich fluids in sedimentary environments in the earth's crust could originate from abiotic sources resulting from high-temperature hydrothermal serpentinization of rocks. Sabatier reaction and water gas shift reactions involving fully oxidized carbon (CO₂ and carbonates) and hydrogen were identified as most probable reaction mechanisms [31]. It is therefore possible that by careful adjustment of reaction conditions, the gases involved in the Sabatier equilibrium reaction above could all be present in the reactor during hydrothermal gasification. Potentially, by using appropriate catalysts and additives, the Sabatier reaction could be tuned to produce either hydrogen or methane or both during hydrothermal gasification of biomass. In essence, the results from the sodium carboxylates strongly support the suggestion that the ruthenium catalyst could influence both hydrogen production and methanation reactions within the same reaction space. Consequently, the kinetics and thermodynamic restrictions of Sabatier reaction under hydrothermal conditions would be an interesting future study.

3.2. Analyses of gasification results by gasification efficiencies

Due to the possibilities of different reactions occurring, especially in the presence of additives, constructing an overall reaction equation and appropriate product balance may be difficult. Often, the weight of additives and their reaction products are usually much larger than other biomass reaction products. Therefore, the contributions of these large components would apparently, give high overall product balances, irrespective of the contributions of, e.g. gas products, tar and char [32]. Hence, attempts have been made to express the overall gasification efficiencies obtained in this work in terms of the gasification of both the reacting carbon and hydrogen atoms in the feed biomass materials.

3.2.1. Carbon gasification

More frequently in literature, carbon gasification efficiency has been used to indicate the overall conversion of biomass during gasification. However, where a carbon-capture agent has been employed, much of the carbon evolved as carbon dioxide will be in solution (e.g. sodium carbonate) or in solid phase (e.g. as calcium carbonate). Hence, CGE could no longer be based only on gaseous carbon products. It is possible to calculate the amount of carbon dioxide produced during experiments with alkaline additives. For experiments with sodium hydroxide, carbon dioxide produced was obtained by determining the inorganic carbon (IC) contents of the

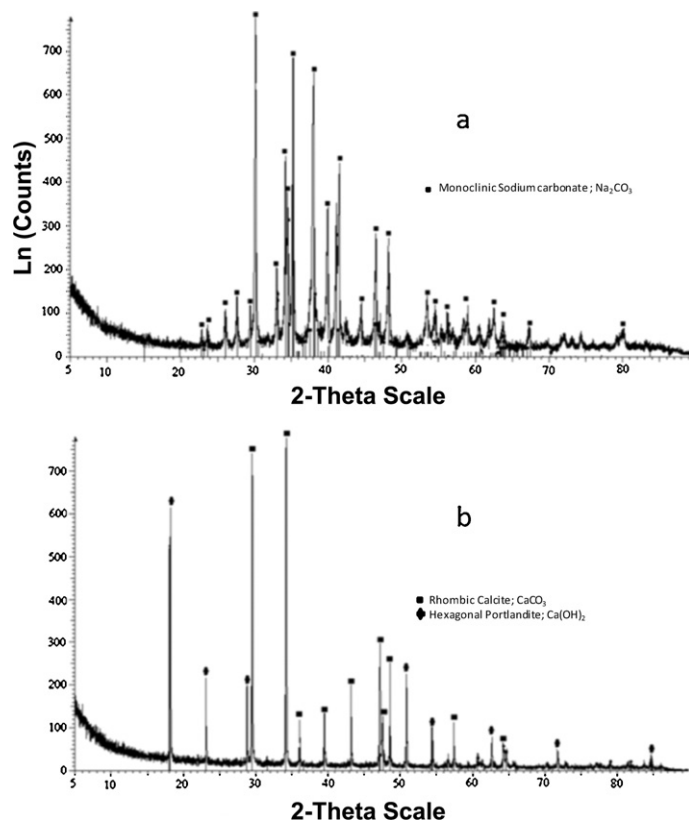


Fig. 6. Thermogravimetric decomposition profiles of insoluble solid residue, plot a: TGA; plot b: Derivative TGA.

aqueous effluents since sodium carbonate is soluble in water. However, for experiments with CaO or calcium hydroxide, the carbon dioxide produced would be converted to insoluble calcium carbonate. XRD analysis of a sample of dried filter cake obtained during the gasification in the presence of CaO is presented in Fig. 6. It shows that the main crystalline compounds in the filter cakes were calcium carbonate and calcium hydroxide. Such inorganic carbon can be determined using TGA analyses of the oven-dried filter cake (insoluble solid). Typical TGA results showed that these solid residues comprised of calcium carbonate and unreacted calcium hydroxide. Fig. 7 displays the TGA thermograms of some filter cakes compared with pure calcium carbonate and calcium hydroxide. The TGA and DTG results shown in Fig. 7 (Plot a and Plot b, respectively) were used to calculate the weight losses due to the evolution of carbon dioxide from calcium carbonate at about 800 °C. Also the weight loss around 500 °C was present in the TGA of calcium hydroxide and all the filter cakes. The losses observed at this temperature were due to the decomposition of the hydroxide leading to the loss of water. The adjusted weight loss due to carbon dioxide evolution from calcium carbonate was used to obtain carbon dioxide and hence the inorganic carbon in these experiments. With these results it was possible to calculate carbon gasification efficiencies (CGE) in this work, which should give a clearer picture of the effect of the additives/catalysts in gas production.

Table 2 presents the carbon gasification results for all the reactions reported in this work. The CGE was expressed as follows;

$$\text{CGE} = \frac{(C_{\text{gas}} \pm C_{\text{IC(aqueous)}} \pm C_{\text{IC(solid)}})}{\text{Carbon amount in the feed}} \times 100\%$$

C_{gas} , is amount of carbon in gas products; $C_{\text{IC (aqueous)}}$, is amount of carbon as inorganic carbon (IC) in aqueous effluent; $C_{\text{IC (solid)}}$, is

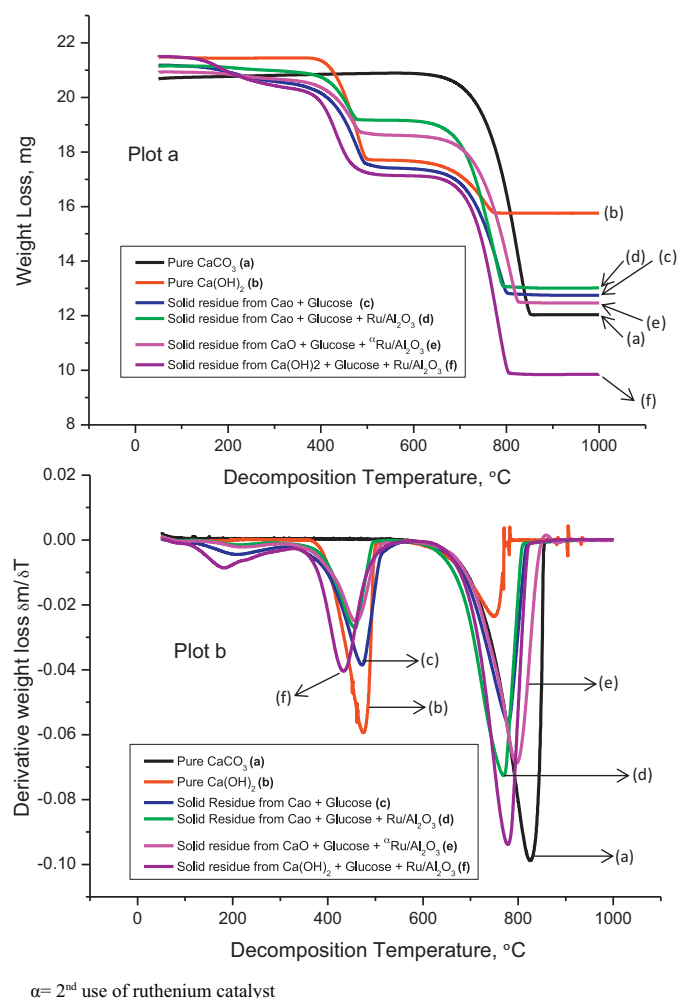


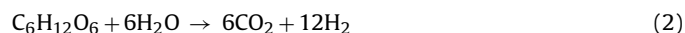
Fig. 7. XRD profiles of selected dried solid residue/filter cake; (a) glucose reacted with NaOH and Ru/Al₂O₃; (b) glucose reacted with CaO and Ru/Al₂O₃.

amount of carbon as inorganic carbon(IC) in solid product (dried filter cake)

Results show that in the absence of catalysts, only 32.3% carbon gasification was achieved, indicating that a greater proportion of carbon was converted to tar and char rather than gas. Except in cases where lower concentrations of sodium hydroxide were used, carbon gasification efficiencies were generally above 90% in the presence of Ru/Al₂O₃. This agrees with the work of several others in literature who reported carbon gasification of over 97% during the supercritical water gasification of different biomass samples using ruthenium catalysts. Ruthenium supported on different supports including carbon and rutile has been reported to give hydrothermal biomass conversions from 97% to 100%, usually at temperatures above 450 °C [33–37].

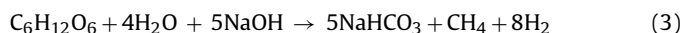
3.2.2. Hydrogen gasification

The ultimate gasification of glucose under supercritical water conditions to produce hydrogen and carbon dioxide only could be represented by;

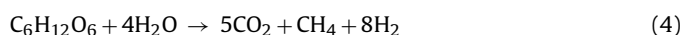


However, in practice, these are not the only products obtained, and this equation cannot account for the production of methane during this process. Results from our work on the alkaline gasification of glucose in the presence of sodium hydroxide at 450 °C, 31 MPa, showed that hydrogen gas and methane were the main

product gases, with high selectivity towards hydrogen [18]. The above equation could then be modified as follows;



This reaction indicates the ability of sodium hydroxide to completely remove carbon dioxide, so that the product gases include mainly hydrogen and methane as earlier reported [16,23,32]. It is important to note that alkalis have also been shown to play roles other than the removal of CO₂, including the decomposition of biomass to relevant intermediates and catalyzing the water gas shift reaction [16,19]. However, if sodium hydroxide is excluded from reaction (3), then the following reaction equation results;

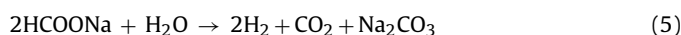


In literature, hydrogen gasification efficiency has often been calculated based on the hydrogen atoms in the biomass only and this could lead to erroneous interpretation of gasification results. In this work, hydrogen gasification efficiencies (HGE) have been calculated using two different expressions as follows;

$$\text{HGE1} = \frac{\text{Mass of hydrogen in gaseous products}}{\text{Mass of hydrogen in biomass}} \times 100\%$$

$$\text{HGE2} = \frac{\text{Mass of hydrogen in gaseous products} \times 100\%}{\text{Mass of hydrogen in reactants (biomass + SR water)}}$$

SR represents the stoichiometric reacting water based on equation (4). Hydrogen gasification efficiencies obtained from these two expressions during this work are presented in Table 3. Unlike carbon gasification, where it is certain that all the carbon atoms come from the biomass, hydrogen gasification efficiencies calculated based on hydrogen atoms of biomass would give inaccurate results. Using the carboxylates as example, it can be seen from Table 3, that hydrogen gasification for sodium formate calculated using HGE1 reached 190%. Similarly, the average hydrogen gasification efficiency for sodium acetate was about 148%. However, by including the hydrogen atoms in the stoichiometric reacting water based on the equations developed in a recent paper [18], the hydrogen gasification efficiencies for both formate and acetate were nearly 100%. This suggested a good prediction of the reaction of these carboxylates in supercritical water due to the apparent simplicity of these reactions.



Based on the reaction products obtained, it can be seen from Table 3 that the HGE1 values are much higher than the HGE2 values. However, unlike the sodium carboxylates, both HGE values for biomass were less than 100%, indicating that reaction Eq. (4) could only be an approximation of the overall reactions occurring in the reactor with real biomass. Although, high carbon gasification efficiencies were achieved with the biomass samples, the HGE values were not as high. It would therefore be reasonable to assume that reactions leading to these lower HGE values did not affect carbon gasification, especially since the feed samples were the only source of carbon atoms. For the carboxylates, the approximation gave a good match of their reactions in terms of hydrogen atoms from feed and stoichiometric reacting water. However, with biomass and biomass model compounds, the reactions involved would be more complicated. For instance, biomass dehydration is a common reaction under thermochemical processes including hydrothermal gasification [16,38]. Such dehydration would lead to loss of biomass-hydrogen as water into an already aqueous medium.

Considering Eq. (4); for glucose, complete reforming of available methane to hydrogen gas would lead to the hypothetical Eq. (2). On

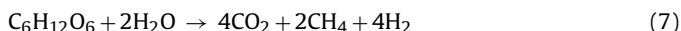
Table 4

Recent results from literature on the batch catalytic SCWG of different biomass feedstock using ruthenium-based catalysts.

Ruthenium-based catalysts	Feed	Feed Load wt %	Temp. °C	^a R. time (min)	H ₂ yield, mol/kg	CH ₄ yield, mol/kg	CGE, %	Source
Ru/TiO ₂	Sugarcane bagasse	3.3	400	15	3.2	8.5	100	Ref [39]
Ru/C	Sugarcane bagasse	3.3	400	15	1.9	15.6	50.3	Ref [39]
Ru/TiO ₂	Cellulose	3.3	400	15	2.8	13.6	74.4	Ref [39]
Ru/γ-Al ₂ O ₃	Glucose	2.0	380	15	18	4.0	45.0	Ref [40]
Ru/γ-Al ₂ O ₃	Glucose	2.0	380	60	33	6.0	78.0	Ref [40]
Ru/C	Glucose	2.0	380	15	17	7.0	64.0	Ref [40]
Ru/C	Glucose	2.0	380	60	26	7.0	80.0	Ref [40]
Ru/γ-Al ₂ O ₃	Cellulose	2.0	380	60	34	5.0	53.0	Ref [40]
Ru/C	Cellulose	2.0	380	60	22	4.0	72.0	Ref [40]
Ru/C	<i>P. tricornutum</i> (algae)	2.5	400	60	2.5	12.9	68.0	Ref [13]
Ru/C	<i>P. tricornutum</i> (algae)	5.1	400	67	1.9	11.8	74.0	Ref [13]
Ru/α-Al ₂ O ₃	Glucose	6.7	550	10	10.8	8.61	96.2	This Work
Ru/α-Al ₂ O ₃ /NaOH	Glucose	6.7	550	10	21.1	8.32	99.1	This Work
Ru/α-Al ₂ O ₃ /CaO	Glucose	6.7	550	10	14.7	12.8	97.5	This Work
Ru/α-Al ₂ O ₃ /CaO	Cellulose	6.7	550	10	9.10	13.1	98.2	This Work
Ru/α-Al ₂ O ₃ /CaO	Xylan	6.7	550	10	10.7	9.43	98.7	This Work
Ru/α-Al ₂ O ₃ /CaO	Sawdust	6.7	550	10	10.4	7.64	99.0	This Work

^a Time of reaction at designated temperature.

the other hand, partial or complete methanation of the carbon dioxide using the available hydrogen gas would lead to the following reaction equations, respectively;



It can therefore be seen that Eqs. (4), (7) and (8) represent decreasing amounts of hydrogen atoms on the feed side of the equation. For instance, a total of 0.11 g of hydrogen was available for gasification in Eq. (4), while Eqs. (7) and (8) have 0.088 g and 0.067 g of hydrogen in the reactants, respectively. These possible reactions would lead to different results in the calculation of hydrogen gasification efficiencies, since the exact contribution of each reaction to hydrogen yield could not be ascertained. This could well be responsible for the lower HGE's obtained in this work compared to CGE. Hence, by careful inspection and analysis of results, reaction Eq. (4) was used to calculate HGE2 values where ruthenium was absent. For catalytic work with the ruthenium catalyst, HGE2 values were calculated based on reaction Eq. (7).

In this work therefore, the discussion on hydrogen gasification will thus be restricted to the HGE2 values, since the HGE2 expression gave more realistic values for the sodium carboxylates. Without any catalysts or additive, hydrogen gasification for glucose was only 6.58%. With the ruthenium catalyst only, HGE increased nearly 10-fold to 64.3% on the average, even though the distribution of the hydrogen atoms changed slightly with repeated catalyst use in favour of hydrogen gas. Significant increase in hydrogen gasification was observed when glucose was reacted in 1.50 M NaOH, both in the presence or absence of Ru/Al₂O₃. Indeed, significantly more HGE value (87%) was obtained when NaOH was combined with Ru/Al₂O₃ than when only NaOH was used, due the increase methane production. In addition, similar value of HGE was found when 1.07 M of CaO was combined with Ru/Al₂O₃. However, in all cases, the distribution of the hydrogen atoms in both hydrogen gas and methane were different. The ratio of hydrogen atoms as hydrogen gas to methane was 9½:1 with 1.50 M NaOH alone. With a combination of 1.50 M NaOH and Ru/Al₂O₃, the ratio became 1½:1. Interestingly, the ratio changed dramatically to 1:1½ in favour of methane when the combination of CaO and Ru/Al₂O₃ was used. These results suggest a potential flexibility in gas product composition during the supercritical water gasification of biomass with Ru/Al₂O₃ in the presence of different alkaline additives.

3.3. Comparison of results with literature

Table 4 presents the summary of results from some recent work in literature on the hydrothermal gasification of different biomass feedstocks using ruthenium-based catalysts in batch reactors. On one hand, results from Haiduc et al. [13] and Osada et al. [39] demonstrated higher selectivity of Ru/C towards methane production compared to hydrogen gas yields. They found no distinction between the product yields at both short (15 min) and long (~60 min) reaction times at the same reaction temperature of 400 °C. On the other hand, results from Azadi et al. [40] shows higher selectivities towards hydrogen compared to methane production, while using both Ru/C and Ru/γ-Al₂O₃ catalysts. Interestingly, their results show that hydrogen yields tended to increase after long (60 min) reaction times whereas methane yield remained fairly stable at 380 °C. Comparing the results of these groups of researchers, the difference in the selectivities of the ruthenium-based catalysts towards either methane or hydrogen as reported could be attributed to the reaction temperature used. It could therefore mean that there exists a transition temperature between 380 °C and 400 °C for the change in selectivities between methane and hydrogen yields.

Results from this present study show that the yields of methane and hydrogen were similar (within ±3 mol/kg of each other), except for the case involving the use of NaOH and the Ru/Al₂O₃ catalyst; where hydrogen yield was more than twice the methane yield. The general trends in hydrogen and methane yields in this present study, compared to the work of Azadi et al. [40], suggest a shift in the catalytic activity of ruthenium to methanation reactions, at the operating temperature of 550 °C. Apart from the result of Osada et al. [39] who achieved 100% carbon gasification (CGE) while using Ru/TiO₂ catalyst for gasification sugarcane bagasse, CGE from other researchers using batch reactors were ≤80%. In this present work, CGE values for tests involving ruthenium-alumina were consistently above 97%, even with the higher feed loading of 6.7 wt% compared to Refs [39,40]. Again, this could be due to the high reaction temperature used. Such high CGE values have been reported for hydrothermal biomass gasification in the presence of ruthenium-based catalysts but only in continuous reactors [35–37,41].

4. Conclusions

A novel process for the production of hydrogen and/or methane from catalytic supercritical water gasification of biomass with a ruthenium-based catalyst has been investigated. The catalyst consisted of ruthenium metal impregnated onto hydrothermally

stable alpha-alumina spheres. The effects of this catalyst on the composition of gas products obtained during supercritical water gasification of various biomass and biomass-related samples have been studied in the presence of alkaline additives. The gasification reactions were conducted at 550 °C, and pressures of 36 MPa in an Inconel batch reactor. Without alkaline additive, Ru/Al₂O₃ almost completely converted glucose into a gas product comprising of carbon dioxide and relatively high yields of hydrogen and methane, with a CGE of 96%.

High concentration of NaOH was more selective towards hydrogen production. Results showed that the selectivity of Ru/Al₂O₃ catalyst towards hydrogen over methane was enhanced in the presence of NaOH and Ca(OH)₂. Conversely, CaO enhanced the selectivity of fresh ruthenium catalyst towards methane formation but with subsequent re-use of the Ru/Al₂O₃, selectivity towards hydrogen increased. Results from other biomass samples gasified with the fresh catalyst showed similar trends as those of glucose, indicating the versatility of the catalyst.

The composition of the gas products obtained from the catalytic and non-catalytic gasification of pure sodium carboxylates (sodium formate and sodium acetate) suggested that the catalyst was effective for methanation reaction as well as methane-reforming for hydrogen production depending on thermodynamic equilibrium. Without the catalyst, sodium formate exclusively produced hydrogen and carbon dioxide, but in its presence significant yield of methane was obtained. In addition, sodium acetate alone produced a gas with a methane/hydrogen mole percent ratio of 6:1. However, in the presence of the catalyst, methane/hydrogen mole percent ratio was approximately 1:1. It could therefore be suggested that in the alkaline hydrothermal environments studied, Ru/Al₂O₃ could effectively catalyze the reversible Sabatier reaction both in the forward and backward direction depending of the concentrations of the relevant gases, i.e. hydrogen, methane, steam and carbon dioxide.

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